<Organic Materials Chemistry> Polymeric Materials

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- Polymeric Materials -

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Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of high-density polymer brushes (HDPB).

Research Activities (Year 2002)

Presentations

Designing New Surfaces by LRP, Fukuda T, and 3 other presentations, Macro Group UK, International Conference on Polymer Synthesis, UK, 29 Jul - 1 Aug.

Mechanism and Kinetics of LRP: Absolute Comparison of Theory and Experiment, Fukuda T, and 2 other presentations, 224th ACS National Meeting, USA, 18 - 22 Aug.

Functionalization of Cellulosics by LRP, Tsujii Y, and 1 other presentation, 1st International Cellulose Conference, Kyoto, 6 - 8 Nov.

6 Presentations, Spring Meeting, Soc. Polym. Sci, Jpn., 29 - 31 May. 2 Presentations, Polymer Symposium, Soc. Polym. Sci. Jpn., 12 Jul. 6 Presentations, Autumn Meeting, Soc. Polym. Sci, Jpn., 2 - 4 Oct.

Grants

Fukuda T, Science and Technology of HDPB, Grant-in-Aid for Science Research. (A)(2), 1 Apr 2002 - 31 Mar 2005.

Fukuda T, Development of Living Radical Emulsion Polymerization, Grant-in-Aid for Science Research. (B)(2), 1 Apr 2000 - 31 Mar 2003.

Tsujii Y, Fundamental Study on HDPB, Grant-in-Aid for Science Research. (B)(2), 1 Apr 2002 - 31 Mar 2005.

Tsujii Y, Development of New Surface-Modifying Technology, Ind. Tech. Research Grant Program from NEDO, 1 Nov 2000 - 31 Mar 2003.

Ohno K, Gold Nanoparticles Coated with HDPB, Grant-in-Aid for Yound Scientists. (B), 1 Apr 2002 - 31 Mar 2004.

Kaya K, Collaboratory on Electron Correlations, Grant-in-Aid for Cre. Sci. Res., 1 Apr 2001 - 31 Mar 2006.

Absolute Comparison of Kinetic Theory and Experiment on Living Radical Polymerizations

Absolute comparison of the kinetic theory and experiment was made for the two main branches of living radical polymerization, i.e., nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP). Figure 1 shows an example, in which the theories (lines) and experiment (circles and squares) on the polymerization rate and polydispersity index for NMP are compared. It is an *absolute* comparison, since the parameters appearing in the theoretical formula have all been determined by independent experiments. Experiment well agrees with theory (Figure 1). This is the first experimental evidence showing that the most fundamental parts of the LRP kinetic theories work on an absolute scale. The result also demonstrates that the addition of conventional initiator such as benzoyl peroxide can not only increase the polymerization rate but also lower the polydispersity, as is predicted by the theory. Similar results were obtained for ATRP, too. The kinetic knowledge obtained in this work is important to design experimental conditions for the highest possible achievement.

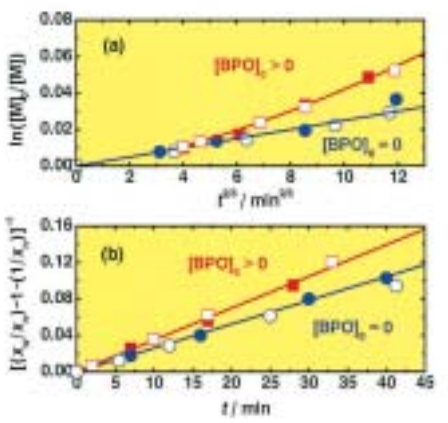

Figure 1. Plot of (a) $\ln([M]_0/[M])$ vs $t^{2/3}$ and (b) $[(x_w/x_n) - 1 - (1/x_n)]^{-1}$ vs t for the styrene/PS-DEPN/(BPO) systems (80 °C): $[PS\text{-}DEPN]_0 = 25$ mM; $[BPO]_0 = 0$ (● and ○) and 4.7 mM , (■ and □), where M is monomer (styrene), PS is polystyrene, DEPN is *N-tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, BPO is benzoyl peroxide, and x_w and x_n are weight- and number-average degrees of polymerization, respectively. The duplicated experiments (circles and squares) well agree with the theoretical (solid and broken) lines calculated with the independently determined rate constants.

Glass Transition Temperatures of High-Density Poly(methyl methacrylate) Brushes

Polymers densely end-grafted on a solid surface will be obliged to stretch away from the surface, forming a so-called "polymer brush". We were the first to succeed in applying atom transfer radical polymerization (ATRP), a variant of living radical polymerization, to the graft polymerization on a solid surface and yielding a polymer brush composed of low-polydispersity polymer with the highest graft density reported to data (ca. 0.7 chains/nm^2). It was previously revealed that in such a graft layer polymer chains were highly extended in a good solvent, nearly to their full length, and the properties of this high-density polymer brush in a good solvent condition are quite different and unpredictable from those of "moderately dense" polymer brushes. However, the properties of this high-density polymer brush in dry state have rarely been characterized. We studied the glass transition temperature (T_g) of the high-density polymer brush for the first time. It was revealed that T_g of the high-density polymer brushes is quite different from that of the cast (ungrafted) films and the difference originates from the characteristic bulk structure/properties of the high-density brushes.

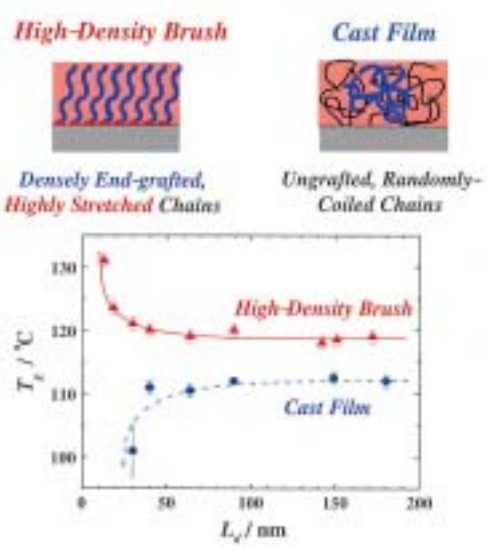

Figure 2. Plots of T_g vs. L_d (film thickness) for the high-density poly(methyl methacrylate)(PMMA) brushes (▲) and the cast (ungrafted) PMMA films (●) measured by temperature-variable spectroscopic ellipsometry. PMMA brushes with a constant graft density (ca. 0.7 chains/nm^2) but differing graft chain lengths (the number-average molecular weight, M_n, $15000 < M_n < 182000$) were prepared by ATRP on a silicon substrate. The cast PMMA films were also prepared on a silicon substrate. The brush and the cast film with nearly the same film thickness have almost the same molecular characteristics. Therefore, the T_g difference between these two types of films arises only from the difference in their film structure.